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SMR.865 - 5

WORKSHOP ON
COMPUTATIONAL METHODS IN
MATERIALS SCIENCE AND ENGINEERING

"Dynamical properties of extended systems from density-functional perturbation theory"

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Dynamical Properties of Extended Systems from Density-Functional Perturbation Theory

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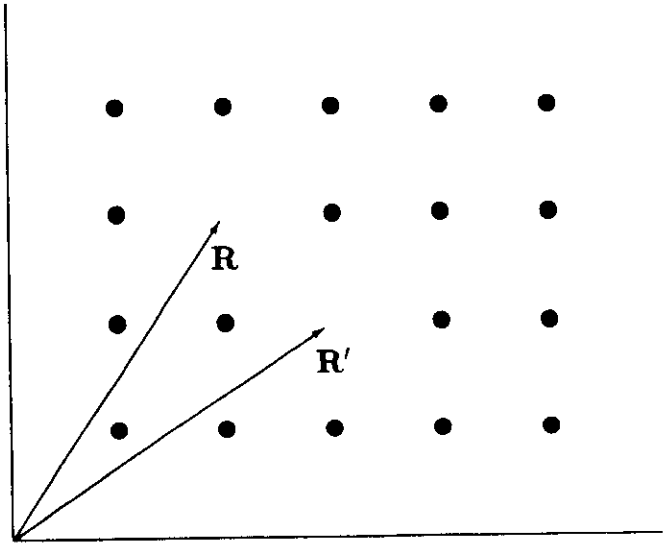
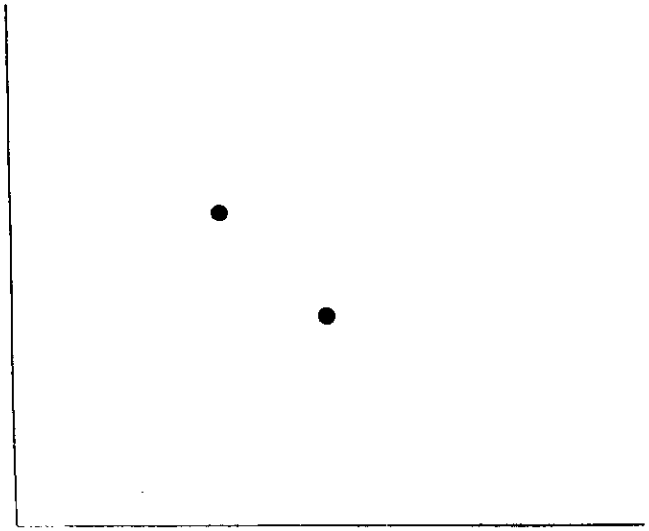
- Lattice dynamics from first principles
- Density-functional perturbation theory
- Lattice dynamics in perfect crystals
- Interatomic force constants
- Lattice dynamics in substitutionally disordered semiconductors
- Perspectives

Phonon Modes



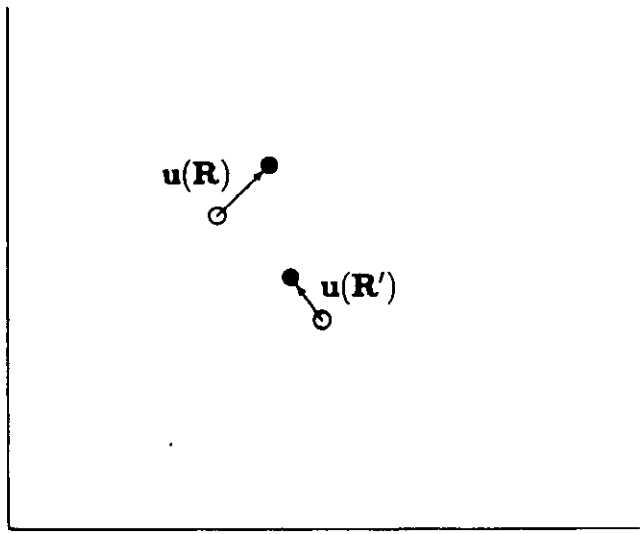


$$V(\mathbf{r}) = \overbrace{\frac{V_0(\mathbf{r})}{\sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R})}}$$

Unperturbed Potential

$$E = E_0$$

Ground-State Energy



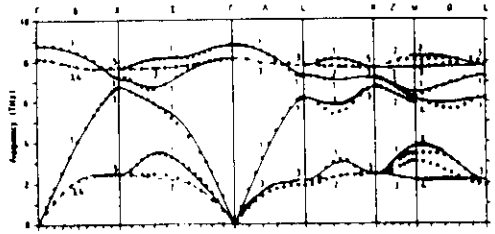
$$V_{[\mathbf{u}]}(\mathbf{r}) = V_0(\mathbf{r}) - \overbrace{\sum_{\mathbf{R}} \mathbf{u}(\mathbf{R}) \cdot \frac{\partial v(\mathbf{r}-\mathbf{R})}{\partial \mathbf{R}}}^{1^{st}\text{ order}}$$

Perturbation due to ion displacements

$$E_{[\mathbf{u}]} = E_0 + \underbrace{\frac{1}{2}\sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}(\mathbf{R}) \cdot \overbrace{\frac{\partial^2 E}{\partial \mathbf{u}(\mathbf{R}) \partial \mathbf{u}(\mathbf{R}')}}^{\mathbf{C}(\mathbf{R}-\mathbf{R}')} \cdot \mathbf{u}(\mathbf{R}')}_{2^{nd}\text{ order}} + \cdots$$

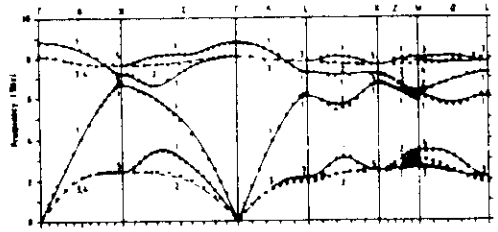
harmonic Approximation

Why Ab-Initio?



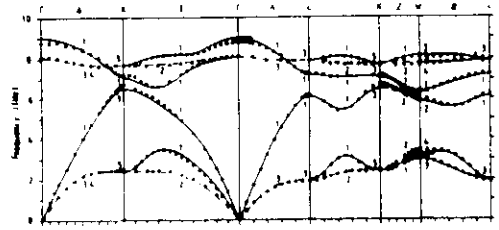
RIM

11 Parameters



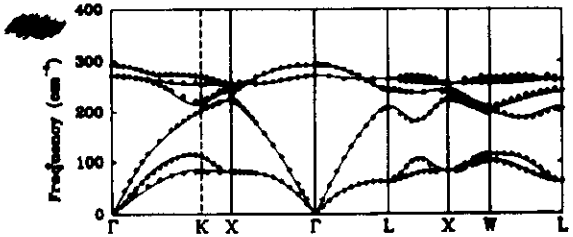
SM

14 Parameters



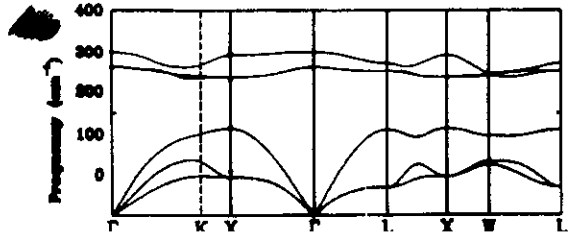
BCM

6 Parameters



Ab-Initio

0 Parameters



Model(???)

Density-Functional Perturbation Theory

$$V_\lambda(\mathbf{r}) = V_0(\mathbf{r}) + \lambda \Delta V(\mathbf{r})$$

$$\frac{\partial E_\lambda}{\partial \lambda} = \int n_\lambda(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}$$

$$\Downarrow$$

$$\frac{\partial^2 E_\lambda}{\partial \lambda^2} = \int \frac{\partial n_\lambda(\mathbf{r})}{\partial \lambda} \Delta V(\mathbf{r}) d\mathbf{r}$$

$$n'_{\lambda=0} = \int \chi(\mathbf{r}, \mathbf{r}') \Delta V(\mathbf{r}') d\mathbf{r}'$$

$$E_\lambda = E_0 + \lambda \overbrace{\int n_{\lambda=0}(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}^{E'_{\lambda=0}} + \frac{1}{2}\lambda^2 \underbrace{\int n'_{\lambda=0}(\mathbf{r}) \Delta V(\mathbf{r}) d\mathbf{r}}_{E''_{\lambda=0}} + \mathcal{O}(\lambda^3)$$

Previous Computational Work

Dielectric Matrices	Direct Approach
● All the excited states of the unperturbed system must be calculated.	● Only occupied states of the perturbed system are needed.
● Much more information must be calculated than physically needed.	● Only needed information is calculated.
● Still, this information is not sufficient to deal with nonlocal perturbations.	● Non local perturbations are easily treated.
● Macroscopic electric fields easily treated.	● Macroscopic electric fields very difficult to treat.
● Computer workload independent of the periodicity of the perturbation.	● Computational workload $\propto \lambda^3$.

Density-Functional Perturbation Theory. II

DFT

$$V_{ext}(\mathbf{r}) \Rightarrow \begin{cases} V_{SCF}(\mathbf{r}) = V_{ext}(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \mu_{xc}(n(\mathbf{r})) \\ \Downarrow \\ (-\nabla^2 + V_{SCF}(\mathbf{r}))\psi_v(\mathbf{r}) = \epsilon_v \psi_v(\mathbf{r}) \\ \Downarrow \\ n(\mathbf{r}) = 2 \sum_{\epsilon_v < \epsilon_F} |\psi_v(\mathbf{r})|^2 \end{cases}$$

DFPT

$$\Delta V_{ext}(\mathbf{r}) \Rightarrow \begin{cases} \Delta V_{SCF}(\mathbf{r}) = \Delta V_{ext}(\mathbf{r}) + \\ \qquad e^2 \int \frac{\Delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \mu'_{xc}(n(\mathbf{r}))\Delta n(\mathbf{r}) \\ \Downarrow \\ (-\nabla^2 + V_{SCF}(\mathbf{r}) - \epsilon_v)\Delta\psi_v(\mathbf{r}) = \\ \qquad (\Delta V_{SCF}(\mathbf{r}) - \langle\psi_v|\Delta V_{SCF}|\psi_v\rangle)\psi_v(\mathbf{r}) \\ \Downarrow \\ \Delta n(\mathbf{r}) = 2 \sum_{\epsilon_v < \epsilon_F} \psi_v^*(\mathbf{r})\Delta\psi_v(\mathbf{r}) \end{cases}$$

Applications to Semiconductor Physics Done So Far

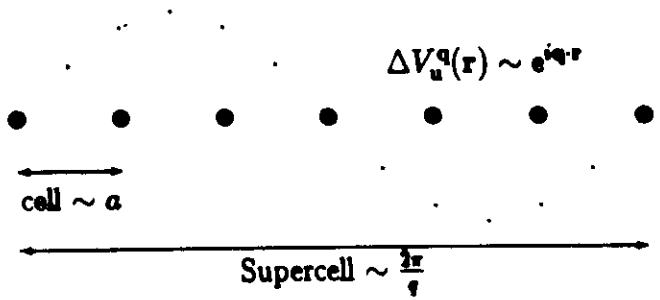
- Dielectric properties.
- Elastic properties.
- Piezoelectric properties.
- Phonon dispersions of pure, bulk crystals.
- Phonon dispersions of surfaces.
- Phonon dispersions of superlattices.
- Phonon dispersions of alloys.
- Raman and infrared activity.
- Thermal expansion.
- Isotopic expansion.
- Anharmonic lifetime of phonons.
- Structural and thermodynamical properties of alloys.
- Electronic properties of interfaces.
- Electronic properties of alloys.

Phonon Modes from DFPT

$$\Delta E[\mathbf{u}] = \frac{1}{2}\sum_{\mathbf{R}\mathbf{R}'}\mathbf{u}(\mathbf{R})\cdot\mathbf{C}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{u}(\mathbf{R}') = \frac{1}{2}\sum_{\mathbf{q}}\mathbf{u}_{\mathbf{q}}^{+}\cdot\tilde{\mathbf{C}}(\mathbf{q})\cdot\mathbf{u}_{\mathbf{q}}$$

$$\mathbf{u}(\mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}}\mathbf{u}_{\mathbf{q}} \longrightarrow \Delta V_{\mathbf{u}}^{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}\Delta V(\mathbf{r})$$

$$\boxed{\tilde{C}(\mathbf{q}) = \int \Delta n_{\mathbf{u}}^{-\mathbf{q}}(\mathbf{r})\Delta V_{\mathbf{u}}^{\mathbf{q}}(\mathbf{r})d\mathbf{r}}$$



To linear order:

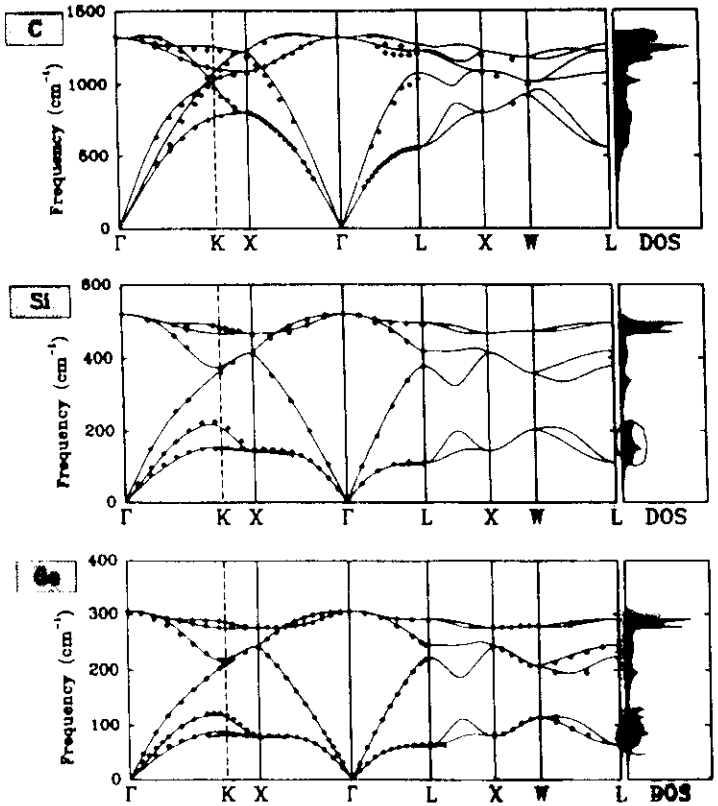
$$\Delta n_{\mathbf{u}}^{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{k},v}\Delta\psi_{\mathbf{k}+\mathbf{q},v}(\mathbf{r})\psi_{-\mathbf{k},v}(\mathbf{r})$$

$$(H_{SCF} - \epsilon_{\mathbf{k},v})|\Delta\psi_{\mathbf{k}+\mathbf{q},v}\rangle = (\Delta V_{SCF,\mathbf{u}}^{\mathbf{q}} - \langle\psi_{\mathbf{k},v}|\Delta V_{SCF,\mathbf{u}}^{\mathbf{q}}|\psi_{\mathbf{k},v}\rangle)|\psi_{\mathbf{k},v}\rangle$$

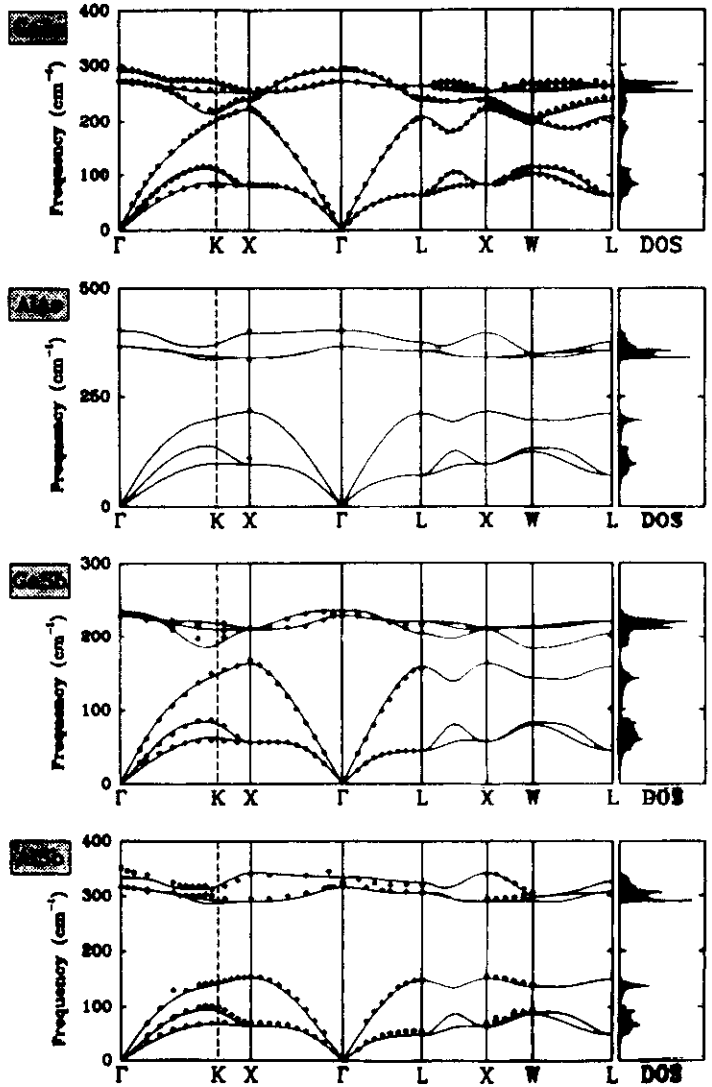
Supercell: CPU $\sim \Omega_{\text{supercell}}^{3}$

DFPT: CPU $\sim \Omega_{\text{cell}}^{3}$

Phonon Dispersions



Phonon Dispersions



Lattice Dynamics and Dielectric Properties of SiO_2 Stishovite

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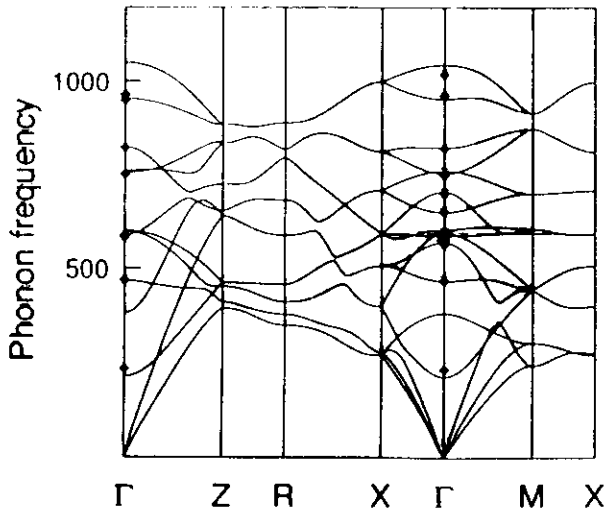
(Received 22 November 1993)

TABLE II. The phonon eigenmodes and the vibrational frequencies of stishovite at Γ. The experimental data are from Ref. [11] for the Raman modes and Ref. [12] for the infrared modes. The frequencies are in cm^{-1}.

Mode	This work	Experiment
	Raman modes	
B_{1g}	214.0	234
E_g	585.4	586
A_{1g}	754.9	751
A_{2g}	599.1	Silent
B_{2g}	954.1	964
	Infrared modes	
B_{1u}	383.6	Silent
E_u (TO)	469.0	470
E_u (LO)	568.9	565
E_u (TO)	595.1	580
E_u (LO)	705.0	700
B_{1u}	761.4	Silent
A_{2u} (TO)	648.8	650
A_{2u} (LO)	1048.5	950
E_u (TO)	821.6	820
E_u (LO)	1043.4	1020



First Principles Linear Response Calculations of Lattice Dynamics for CuCl

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(Received 19 October 1993)

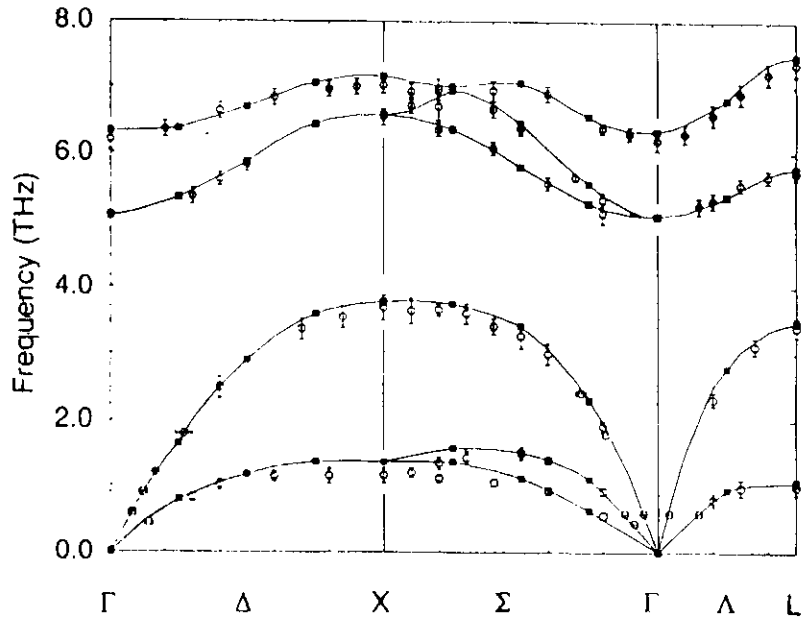

FIG. 1. Phonon dispersion curves of CuCl.

Ab Initio Calculation of Surface Phonons in GaAs(110)

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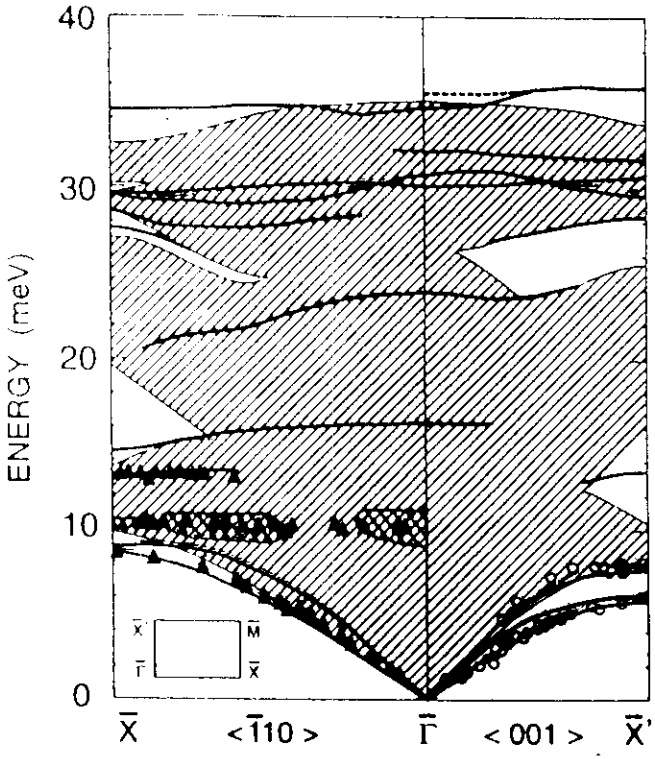
(Received 5 October 1993)



Linear-Response Calculations of Electron-Phonon Interactions

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(Received 3 September 1993)

A new, generally applicable method is developed for *ab initio* calculation of the wave-vector dependent electron-phonon coupling. The screening of the one-electron potential is evaluated by linear-response theory using the local-density approximation and linear muffin-tin orbitals. We calculate electron-phonon coupling strengths and transport properties in Al and, for the first time, in Nb and Mo. Our results are consistent with the experimental results and are compared with previous theoretical results.

PACS numbers: 63.20.Kr, 71.10.+x, 72.15.Eb

The electron-phonon interaction is decisive for many properties of metals [1], such as the electrical and thermal resistivities, superconductivity, and the renormalization of the linear electronic specific heat. In the strong-coupling theory of superconductivity [2], a central quantity is the electron-phonon spectral distribution function $\alpha^2F(\omega)$ and its first reciprocal moment λ. The problem to calculate λ *ab initio* is important, in particular, for quantitative understanding of high-temperature superconductivity. The purpose of this Letter is to develop a new generally applicable method for calculating this quantity which essentially amounts to the self-consistent finding of the full low-energy excitation spectrum of the metal: the quasiparticle energies $E_{\mathbf{k}j}$ and the phonon frequencies $\omega_{\mathbf{q}\nu}$. The most popular estimate of $E_{\mathbf{k}j}$ is the one-electron band structure obtained from a density-functional calculation in the local-density approximation (LDA) [3].

Many previous attempts to compute λ, in particular for transition metals, focused on calculating merely the so-called electronic contribution [4], while the phonon frequencies and eigenvectors were usually taken from inelastic neutron-scattering data and the self-consistent adjustment of the one-electron potential to the phonon distortion was replaced by rigid-ion [5] or rigid-muffin-tin [6] approximations (RIA or RMTA). That these approximations are not justified in general was shown for the case of aluminium by Winter [7] using linear-response theory for the screening.

Accurate phonon frequencies and eigenvectors, as well as the self-consistent screening and, hence, the electron-phonon interaction, may however, be calculated with the frozen-phonon total-energy approach using supercells, but only for commensurate phonon wave vectors q [8–11]. With the crude sampling allowed by the limited size of the supercell, the accuracy of q-integrated quantities like λ is usually not high enough for estimating for instance T_c.

An efficient linear-response technique based on the solid-state Sternheimer method [12] was recently developed and shown to produce accurate phonon dispersions and eigenvectors for arbitrary q in transition metals [13]. The important advantage of this method over that of Baroni *et al.* [12] that systems with narrow bands such as d bands are treated as easily as systems with only broad bands because it uses muffin-tin, rather than plane-wave, basis sets for the electron wave functions. In the present Letter, we generalize this method to the computation of the wave-vector dependent electron-phonon coupling. The screening potential for every q is found self-consistently without the use of any RMTA or RIA. $\alpha^2F(\omega)$ and λ are obtained by integration over the whole Brillouin zone. We demonstrate the applicability of this all-electron approach by computing $\alpha^2F(\omega)$ for a few elemental metals, the sp-band metal Al and for the d-band metals Nb and Mo. Moreover, we present the results for the transport properties: the dimensionless λ_{tr} as well as the phonon-limited electrical and thermal resistivities at 273 K. For the d-band metals, these are the first fully screened *ab initio* calculations.

Our method employs the expression [14]

$$\alpha^2F(\omega) = \frac{1}{2\pi N(0)} \sum_{\mathbf{q}\nu} \frac{\gamma_{\mathbf{q}\nu}}{\omega_{\mathbf{q}\nu}} \delta(\omega - \omega_{\mathbf{q}\nu}), \qquad (1)$$

for $\alpha^2F(\omega)$ in terms of the phonon linewidths $\gamma_{\mathbf{q}\nu}$ arising from the electron-phonon interaction. Here, and in the following, we use atomic Rydberg units, $\sum_{\mathbf{q}}$ means the average over the Brillouin zone (BZ), ν numerates the phonon branches, and $N(0)$ is the electronic density of states per atom and per spin at the Fermi level. The linewidths are given by the Fermi "golden rule" which, when the energy bands around the Fermi level are linear in the range of the phonon energies, may be written as

$$\gamma_{\mathbf{q}\nu} = 2\pi\omega_{\mathbf{q}\nu} \sum_{\mathbf{k}jj'} \delta(E_{\mathbf{k}j})\delta(E_{\mathbf{k}+\mathbf{q}j'}) |g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j}|^2, \qquad (2)$$

where j and j' are the band indices, $E_{\mathbf{k}j}$ are the energies with respect to the Fermi level, and $g^{\mathbf{q}\nu}_{\mathbf{k}+\mathbf{q}j',\mathbf{k}j}$ is the electron-phonon matrix element. The standard definition of g is simply the probability of scattering from the one-electron state $|\mathbf{k}j\rangle$ to the state $|\mathbf{k}+\mathbf{q}j'\rangle$ via the phonon $\mathbf{q}\nu$. In a case like ours, where the electronic states are approximated by superpositions of atom-centered orbitals, it is inconvenient to evaluate this expression because it involves the orbitals at the equilibrium atomic

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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1994 issue.

COMMUNICATIONS

Vibrational and dielectric properties of C_{60} from density-functional perturbation theory

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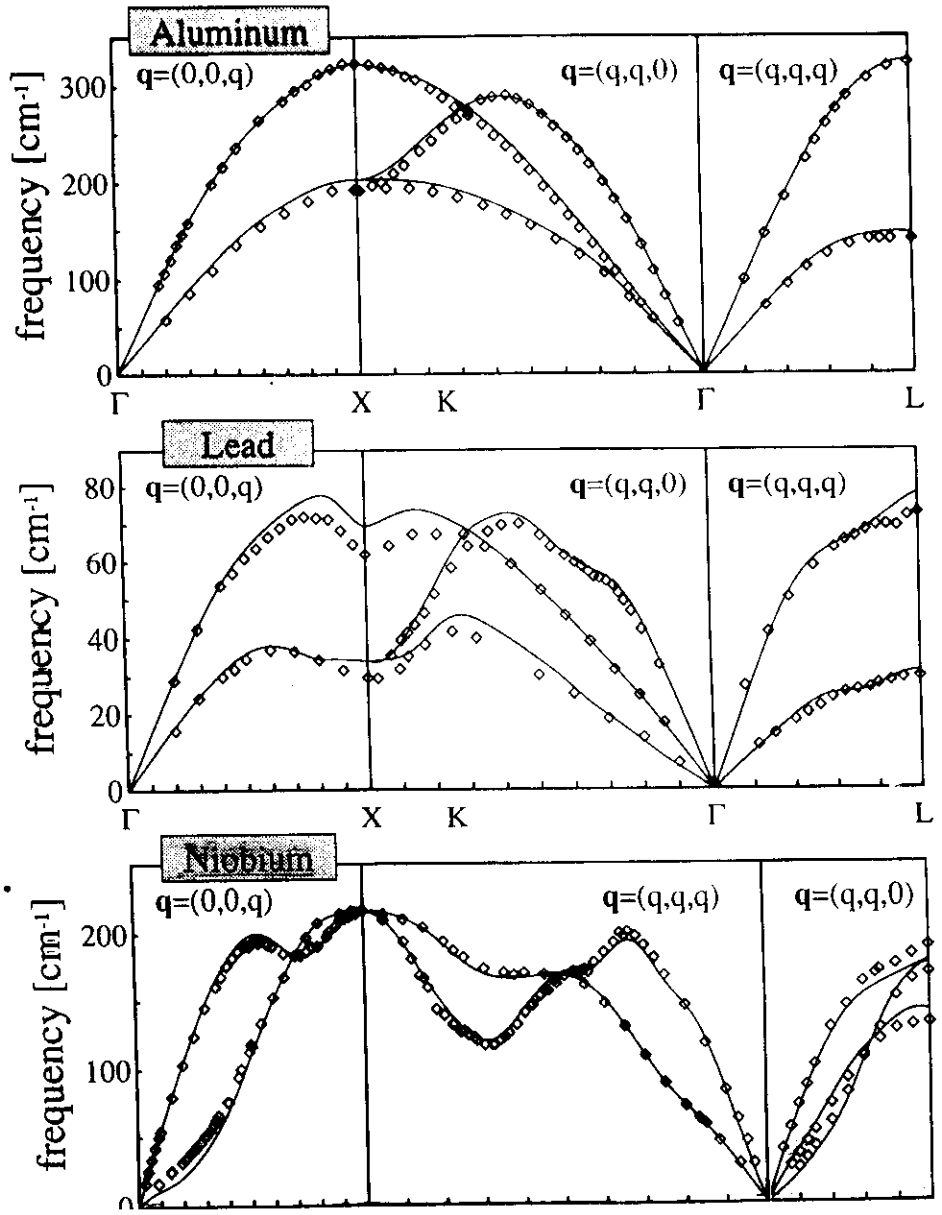
(Received 26 January 1994; accepted 17 March 1994)

The vibrational frequencies and electric polarizability of the C_{60} molecule, both in the gaseous and in the solid phases, are calculated from first principles using density-functional perturbation theory. This method also allows us to obtain the infrared and Raman activities which had never been calculated before. Our results are in excellent agreement with existing experimental data, and they provide accurate predictions for those quantities (such as silent-mode frequencies and vibrational eigenvectors) which are not easily accessible to experiments.

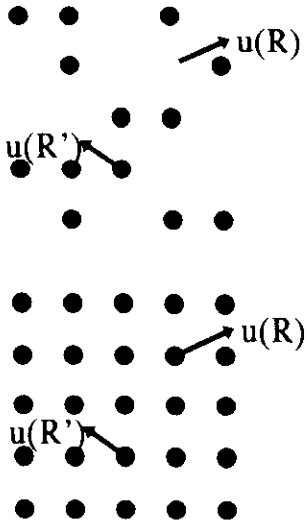
	Expt.	Theory	Label	f	$r_{\parallel}$
R	270	259	H_g	0	0.09
R	431	425	H_g	0	$\simeq 0$
R	493	495	A_g	0	0.23
IR	527	527	F_{1u}	1.00	0
IR	576	586	F_{1u}	0.63	0
R	708	711	H_g	0	$\simeq 0$
R	773	783	H_g	0	0.04
R	1099	1120	H_g	0	0.04
IR	1183	1218	F_{1u}	0.36	0
R	1248	1281	H_g	0	0.01
R	1426	1450	H_g	0	$\simeq 0$
IR	1428	1462	F_{1u}	0.57	0
R	1470	1504	A_g	0	1.00
R	1575	1578	H_g	0	0.37

0021-9606/94/100(11)/8537/3/$6.00



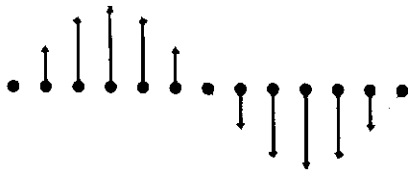
Interatomic Force Constants

$$\mathbf{D}(\mathbf{R},\mathbf{R}') = \frac{1}{\sqrt{M(\mathbf{R}),M(\mathbf{R}')}}\mathbf{\Phi}(\mathbf{R},\mathbf{R}')$$



$$\mathbf{\Phi}(\mathbf{R},\mathbf{R}') = \frac{\partial^2 \mathcal{E}}{\partial \mathbf{u}(\mathbf{R})\partial \mathbf{u}(\mathbf{R}')}$$

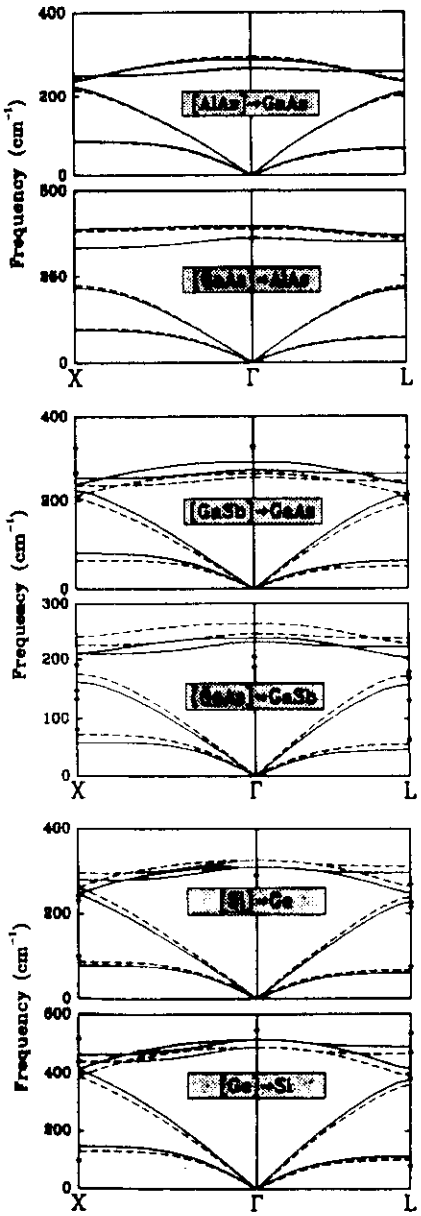
$$\mathbf{\Phi}(\mathbf{R},\mathbf{R}') = \mathbf{\Phi}(\mathbf{R}-\mathbf{R}') = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}\tilde{\mathbf{\Phi}}(\mathbf{q})$$

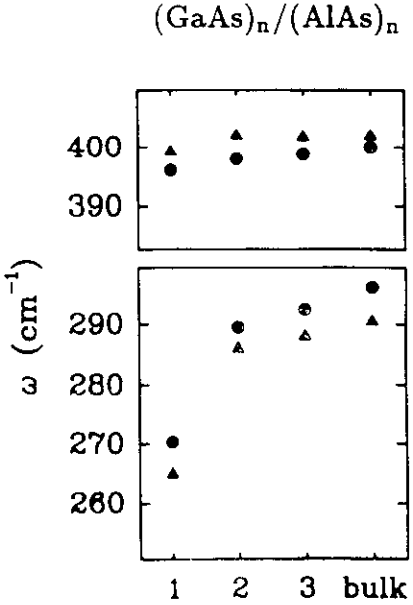


$$\mathbf{u}(\mathbf{R}) \propto e^{i\mathbf{q}\cdot\mathbf{R}} \Rightarrow \begin{cases} \Delta V_{\mathbf{q}}(\mathbf{r}) \\ \Delta n_{\mathbf{q}}(\mathbf{r}) \end{cases}$$

$$\tilde{\mathbf{\Phi}}(\mathbf{q}) = \underbrace{\int \Delta V_{\mathbf{q}}(\mathbf{r})\Delta n_{\mathbf{q}}(\mathbf{r})d\mathbf{r}}_{\text{from Density-Functional Perturbation Theory}} + \mathbf{\Phi}_{\text{ion-ion}}$$

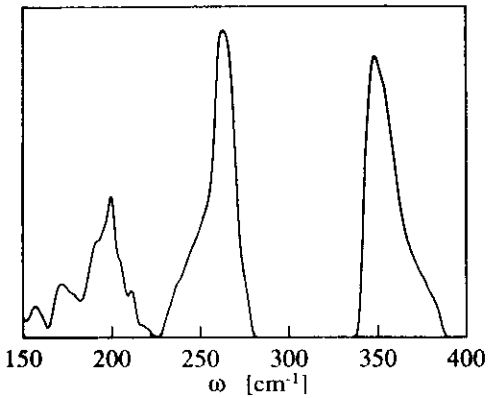
Validity of the Mass Approximation





Phonon DOS vs. Raman Cross section

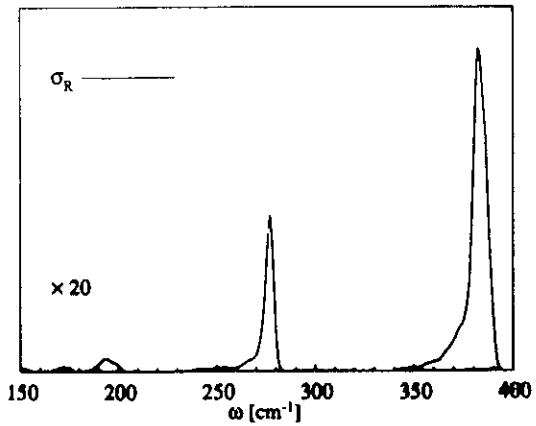
$Ga_xAl_{1-x}As$



$$n(\omega) = \sum_{\nu} \delta(\omega - \omega_\nu)$$

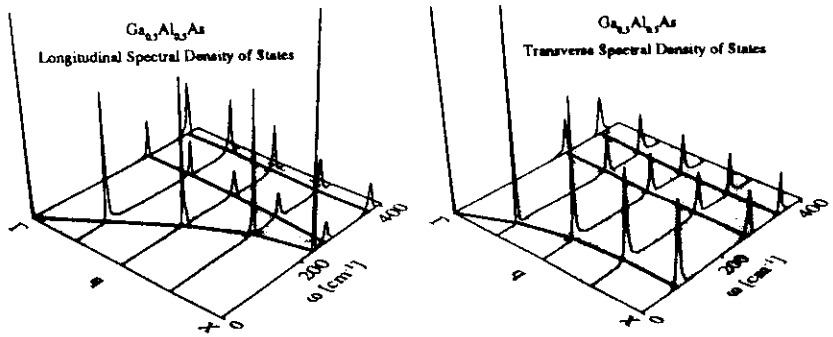
$$\sigma_R^{IF}(\omega) \propto \sum_{\nu} \frac{\delta(\omega-\omega_\nu)}{\omega_\nu} \underbrace{\left| \hat{\epsilon}_F^* \cdot \frac{\partial \overleftrightarrow{\chi}}{\partial q_\nu} \cdot \hat{\epsilon}_I \right|^2}_{A_\nu \approx \langle \Psi_\nu | P_\Gamma | \Psi_\nu \rangle}$$

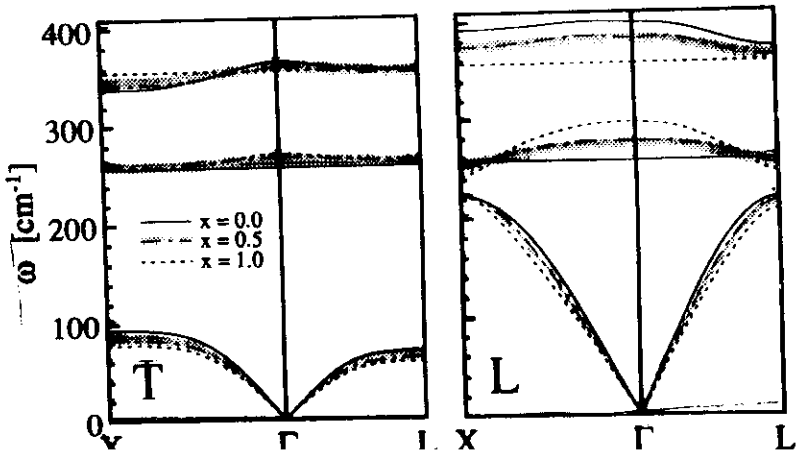
$$\propto n(\omega) A(\omega)$$



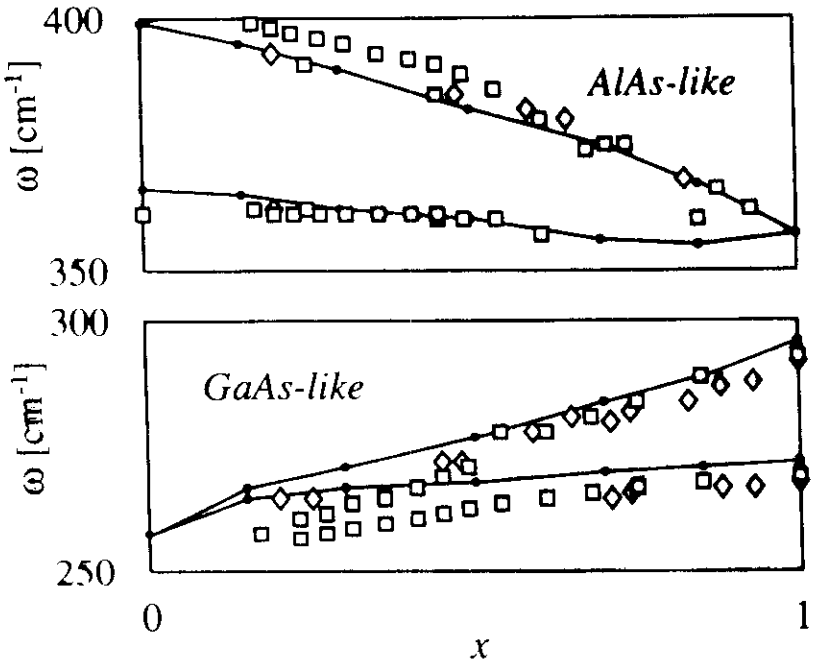
Alloy Phonon Dispersions

$$n_\alpha(\omega, \mathbf{q}) = \sum_{\nu,s} \delta(\omega - \omega_\nu) |\langle \mathbf{q}, \alpha, s | \xi_\nu \rangle|^2$$

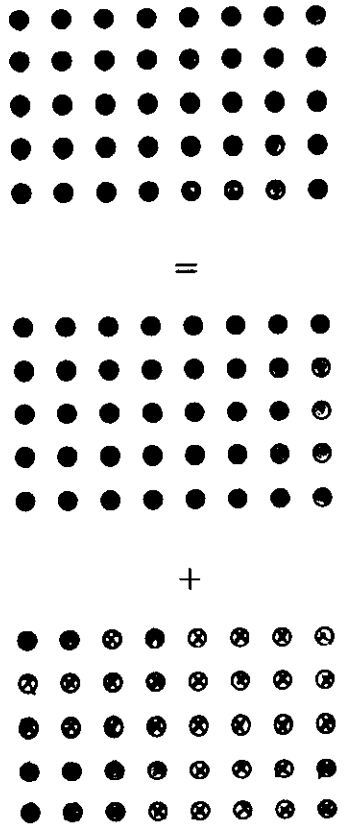




Concentration Dependence of Raman Peaks



Substitutionally Disordered Semiconductors from Perturbation Theory



$V_C(\mathbf{r}) \rightarrow n_C(\mathbf{r})$
$\rightarrow E_C$
$\rightarrow \text{Any}_C$

=

$V_0(\mathbf{r}) \rightarrow n_0(\mathbf{r})$
$\rightarrow E_0$
$\rightarrow \text{Any}_0$

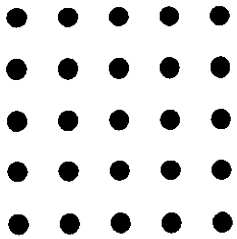
+

$\Delta V(\mathbf{r}) \rightarrow \Delta n(\mathbf{r})$
$\rightarrow \Delta E$
$\rightarrow \Delta\text{Any}$

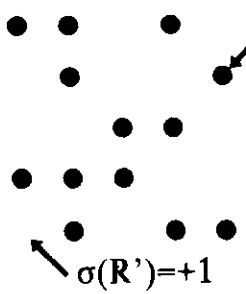
$$\text{Any}_C = \text{Any}_0 + \Delta\text{Any}$$

Stefano Baroni SISSA-Trieste

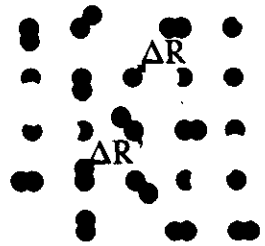
Beyond the Mass Approximation
Higher-Order Interatomic Force Constants



$$\Phi(\mathbf{R},\mathbf{R}') = \Phi(\mathbf{R}-\mathbf{R}')$$

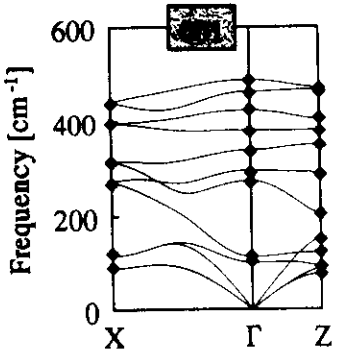


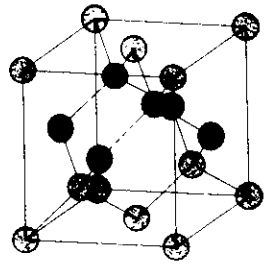
$$\Phi(\mathbf{R},\mathbf{R}') \approx \Phi(\mathbf{R}-\mathbf{R}') + \sum_{\mathbf{R}''} \frac{\partial \Phi(\mathbf{R},\mathbf{R}')}{\partial \sigma_{\mathbf{R}''}} \sigma_{\mathbf{R}''}$$

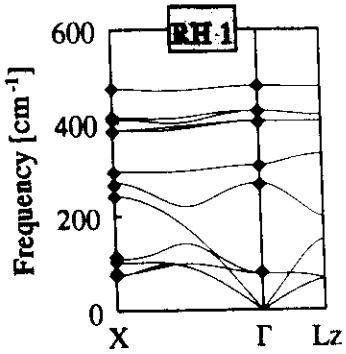


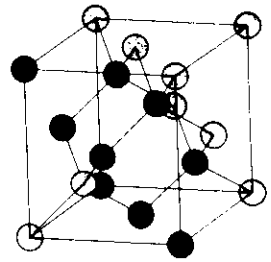
$$\Phi(\mathbf{R},\mathbf{R}') \approx \Phi(\mathbf{R}-\mathbf{R}') + \sum_{\mathbf{R}''} \frac{\partial \Phi(\mathbf{R},\mathbf{R}')}{\partial \sigma_{\mathbf{R}''}} \sigma_{\mathbf{R}''} + \sum_{\mathbf{R}''} \frac{\partial \Phi(\mathbf{R},\mathbf{R}')}{\partial u_{\mathbf{R}''}} \Delta\mathbf{R}''$$

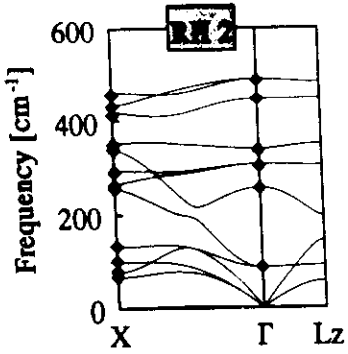
Higher-Order Interatomic Force Constants. II

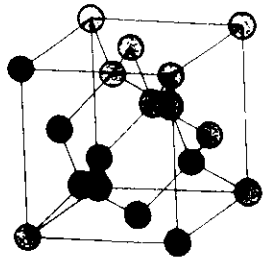












Structural and Electronic Properties of Semiconductor Alloys and Superlattices from Computational Alchemy

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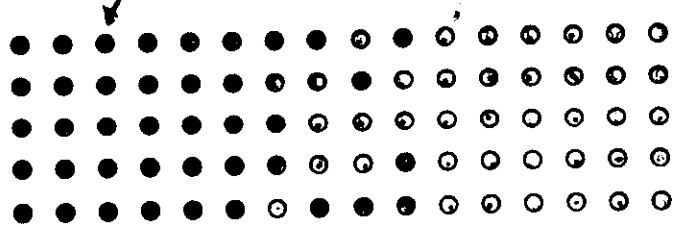
Trieste, Italy

- Computational alchemy: a perturbative approach to the properties of semiconductor alloys and superlattices.
- Density-functional perturbation theory.
- Structural properties of semiconductor alloys and superlattices.
- Band offsets at semiconductor heterojunctions.
- Conclusions.

Pseudopotential Alchemy

$\underbrace{X(\mathbf{R}) = A,\ \ \sigma = +1}$ $\qquad$ $\underbrace{X(\mathbf{R}) = B,\ \ \sigma = -1}$



$$V_C(\mathbf{r}) = \sum_{\mathbf{R}} v_{X(\mathbf{R})}(\mathbf{r} - \mathbf{R})$$

$$= \overbrace{\sum_{\mathbf{R}} \frac{1}{2}\left(v_A(\mathbf{r} - \mathbf{R}) + v_B(\mathbf{r} - \mathbf{R})\right)}^{V_0(\mathbf{r})} +$$

$$\underbrace{\sum_{\mathbf{R}} \sigma(\mathbf{R}) \overbrace{\frac{1}{2}\left(v_A(\mathbf{r} - \mathbf{R}) - v_B(\mathbf{r} - \mathbf{R})\right)}^{\Delta v(\mathbf{r})}}_{\Delta V(\mathbf{r})}$$

$$\Delta n(\mathbf{r}) = \sum_{\mathbf{R}} \sigma(\mathbf{R}) \Delta n_{\mathrm{loc}}(\mathbf{r} - \mathbf{R}) + \mathcal{O}(\Delta v)^2$$

Mapping the Alloy onto a Lattice Gas

$$\Delta V(\mathbf{r}) = \sum_{\mathbf{R}} \sigma(\mathbf{R}) \Delta v(\mathbf{r} - \mathbf{R})$$

$$\Downarrow$$

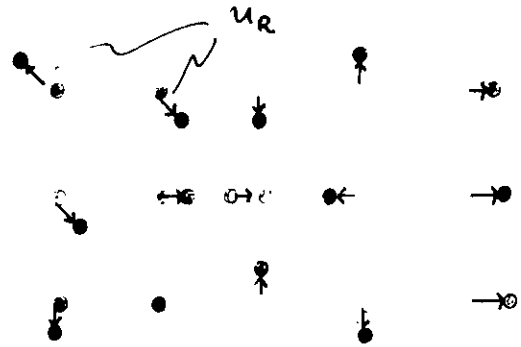
$$n'_{\lambda=0}(\mathbf{r}) = \sum_{\mathbf{R}} \sigma(\mathbf{R}) \Delta n_{\rm loc}(\mathbf{r} - \mathbf{R})$$

$$E'_{\lambda=0} = \sum_{\mathbf{R}} \sigma(\mathbf{R}) \overbrace{\int n_0(\mathbf{r}) \Delta v(\mathbf{r} - \mathbf{R})}^{K}$$

$$E''_{\lambda=0} = \sum_{\mathbf{R}\mathbf{R}'} \sigma(\mathbf{R}) \sigma(\mathbf{R}') \underbrace{\int \Delta v(\mathbf{r} - \mathbf{R}) \Delta n_{\rm loc}(\mathbf{r} - \mathbf{R}) d\mathbf{r}}_{J(\mathbf{R} - \mathbf{R}')}$$

$$\boxed{E \approx E_0 + NK\langle\sigma\rangle + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} J(\mathbf{R} - \mathbf{R}') \sigma(\mathbf{R}) \sigma(\mathbf{R}')}$$

Including Lattice Relaxation



$$\{\mathbf{u}_{\mathbf{R}}\} \propto \Delta v + \mathcal{O}(\Delta v^2)$$

$$\begin{aligned} E[\{\sigma_{\mathbf{R}}\}, \{\mathbf{u}_{\mathbf{R}}\}] = \overline{E} &+ \mu \sum_{\mathbf{R}} \sigma_{\mathbf{R}} + \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \sigma_{\mathbf{R}} \sigma_{\mathbf{R}'} J(\mathbf{R} - \mathbf{R}') \\ &+ \frac{1}{2} \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}_{\mathbf{R}} \cdot \mathbf{\Phi}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{u}_{\mathbf{R}'} \\ &- \sum_{\mathbf{R}\mathbf{R}'} \mathbf{u}_{\mathbf{R}} \cdot \mathbf{F}(\mathbf{R} - \mathbf{R}') \, \sigma_{\mathbf{R}'} \\ &+ \mathcal{O}(\Delta v^3) \end{aligned}$$

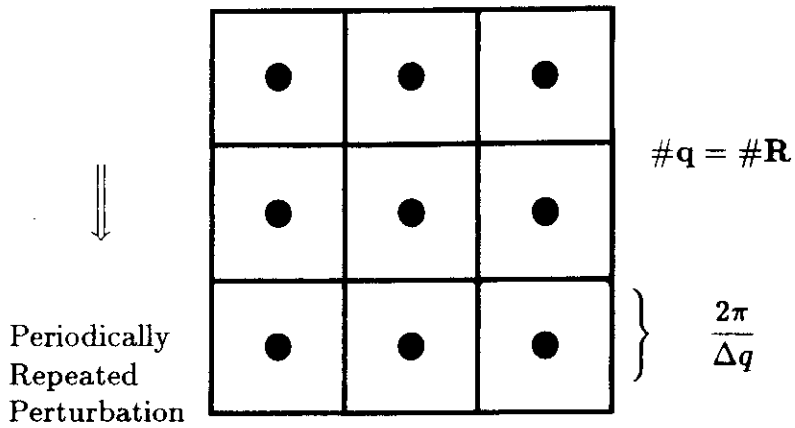
$$\frac{\partial E}{\partial \mathbf{u}_{\mathbf{R}}} = 0 \quad \Longrightarrow \quad \sum_{\mathbf{R}'} \mathbf{\Phi}(\mathbf{R} - \mathbf{R}') \cdot \mathbf{u}_{\mathbf{R}'} = \sum_{\mathbf{R}'} \mathbf{F}(\mathbf{R} - \mathbf{R}') \sigma'_{\mathbf{R}}$$

$$\begin{aligned} \tilde{J}(\mathbf{R} - \mathbf{R}') = J(\mathbf{R} - \mathbf{R}') \\ + \sum_{\mathbf{R}''\mathbf{R}'''} \mathbf{F}(\mathbf{R} - \mathbf{R}'') \cdot \mathbf{\Phi}^{-1}(\mathbf{R}'' - \mathbf{R}''') \cdot \mathbf{F}(\mathbf{R}''' - \mathbf{R}') \end{aligned}$$

Linear-Response Calculation of the Interaction Constants

$$\Delta v(\mathbf{r}) \xrightarrow{\text{LRT}} \Delta n(\mathbf{r})$$

$$\Delta v = \begin{cases} \text{ion substitution}: & \Delta v_S \rightarrow \Delta n_S \\ \text{ion displacement}: & \Delta \boldsymbol{v}_D \rightarrow \Delta \boldsymbol{n}_D \end{cases}$$



○ $$J(\mathbf{R}-\mathbf{R}') = \int \Delta v_S(\mathbf{r}-\mathbf{R})\Delta n_S(\mathbf{r}-\mathbf{R}')\, d\mathbf{r}$$

○ $$\Phi(\mathbf{R}-\mathbf{R}') = \int \Delta \boldsymbol{v}_D(\mathbf{r}-\mathbf{R})\Delta \boldsymbol{n}_D(\mathbf{r}-\mathbf{R}')\, d\mathbf{r}$$

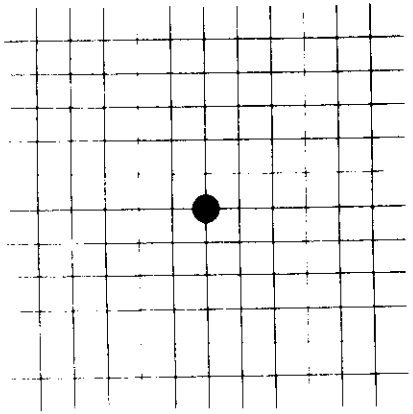
○ $$\mathrm{F}(\mathbf{R}-\mathbf{R}') = \int \Delta \boldsymbol{v}_D(\mathbf{r}-\mathbf{R})\Delta n_S(\mathbf{r}-\mathbf{R}')\, d\mathbf{r}$$
$$= \int \Delta v_S(\mathbf{r}-\mathbf{R})\Delta \boldsymbol{n}_D(\mathbf{r}-\mathbf{R}')\, d\mathbf{r}$$

● $\mathrm{CPU}_{\mathrm{LRT}} \propto \#\mathbf{q} = \#\mathbf{R}$

• Long-range interactions (large # $\mathbf{R}$) tractable!

Reciprocal-Space Formalism

Isolated Perturbation



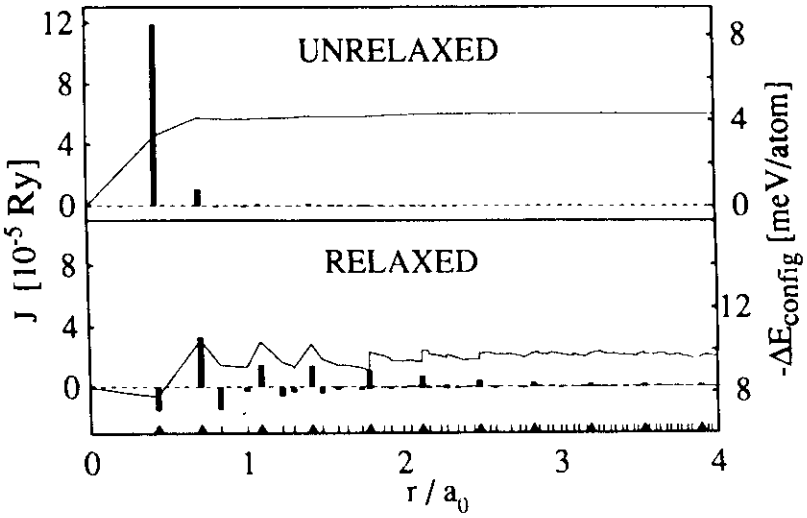
$$\Delta v(\mathbf{r}) = \sum_{\mathbf{q}\in \mathrm{BZ}} \overbrace{e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \Delta\tilde{v}(\mathbf{q}+\mathbf{G})}^{\Delta v_{\mathbf{q}}(\mathbf{r})}$$

$$\Delta n(\mathbf{r}) = \sum_{\mathbf{q}\in \mathrm{BZ}} \overbrace{e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \Delta\tilde{n}(\mathbf{q}+\mathbf{G})}^{\Delta n_{\mathbf{q}}(\mathbf{r})}$$

$$\Delta\tilde{n}(\mathbf{q}+\mathbf{G}) = -\frac{4}{N\Omega} \sum_{cv,\mathbf{k}} \frac{\langle v,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\rangle\langle c,\mathbf{k}+\mathbf{q}|\Delta v_{\mathbf{q}}|v,\mathbf{k}\rangle}{\epsilon_c(\mathbf{k}+\mathbf{q}) - \epsilon_v(\mathbf{k})}$$

- $\mathrm{CPU}_{\mathrm{SCF}} \propto (\#\mathbf{R})^3$

Real-Space Interaction Constants (Si_xGe_{1-x})



Calculated Formation Enthalpies

$Si_x Ge_{1-x}$

Structure	Unrelaxed		Relaxed	
	LRT	SCF	LRT	SCF
ZB	-6.4	-6.5	-6.4	-6.5
$[001]_{2+2}$	-4.6	-4.6	-9.4	-9.7
$[001]_{3+1}$	-3.9	-3.9	-6.3	-6.4
$[001]_{1+3}$	-3.9	-3.9	-6.3	-6.5
$[001]_{3+3}$	-3.1	-3.2	-9.2	-9.5
$[111]_{2+2\ R1}$	-5.9	-5.7	-9.9	-10.0
$[111]_{2+2\ R2}$	-2.5	-2.5	-6.1	-6.3
$[111]_{3+3}$	-2.9	-3.0	-7.6	-7.9
$[110]_{2+2}$	-2.7	-2.7	-10.4	-10.7
$[110]_{3+1}$	-2.5	-2.5	-7.5	-7.8
$[110]_{1+3}$	-2.5	-2.5	-7.5	-7.9

(meV/atom)

$Ga_x In_{1-x} P$

Structures		Bulk (a)			Epitaxial (b)		
	x_{Ga}	a_0	ΔH		$a_\perp$	ΔH	
$SL[001]_{1+1}$	1/2	10.61	21.4	(20.5)	10.61	0.8	(-0.2)
Luzonite	3/4	10.42	16.2	(18.1)	10.25	-0.9	(1.0)
Luzonite	1/4	10.79	16.8	(13.7)	10.96	1.9	(-1.1)
Chalcopyrite	2/4	10.60	10.2	(8.4)	10.60	-10.2	(-12.0)
Famatinite	3/4	10.42	9.1	(10.8)	10.25	-6.9	(-5.4)
Famatinite	1/4	10.79	11.8	(8.2)	10.97	-3.2	(-6.8)
$SL[111]_{1+1}$	1/2	10.61	31.1	(30.4)	10.63	10.6	
Random	0.5	10.60	18.3		10.61	-2.3	
α-phase	12/16	10.42	7.5	(8.6)	10.24	-8.8	
β-phase	26/32	10.36	6.2		10.16	-9.7	

TP$_\mu$ Monte Carlo Simulations
Si_xGe_{1-x}

Sampling $W_{\mu}(\{\sigma\},\Omega) \propto e^{-\frac{1}{k_B T}\left(\Delta E(\{\sigma\},\Omega) + \mu N_\Omega - \mu N_{(\sigma)}\right)}$ ...

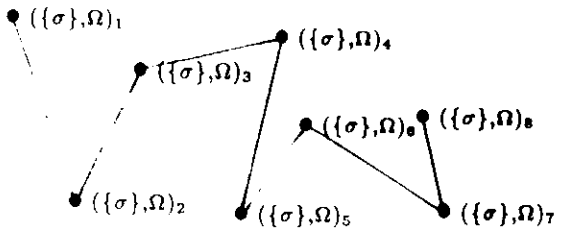
Alloy formation energy:

$$\Delta E(\{\sigma\},\Omega) = E(\{\sigma\},\Omega) - \left(xE_{Si}(\Omega_{Si}) + (1-x)E_{Ge}(\Omega_{Ge})\right)$$

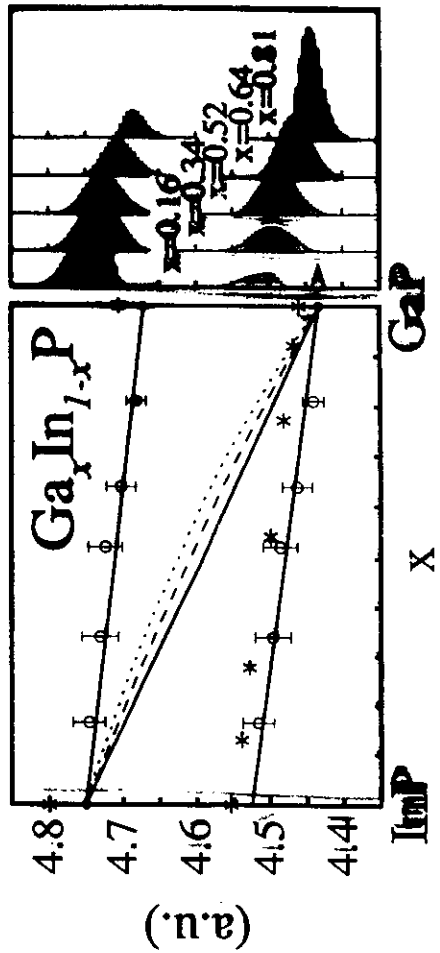
$$= \overbrace{x\left(E_{Si}(\Omega) - E_{Si}(\Omega_{Si})\right) + (1-x)\left(E_{Ge}(\Omega) - E_{Ge}(\Omega_{Ge})\right)}^{\text{Elastic energy}}$$

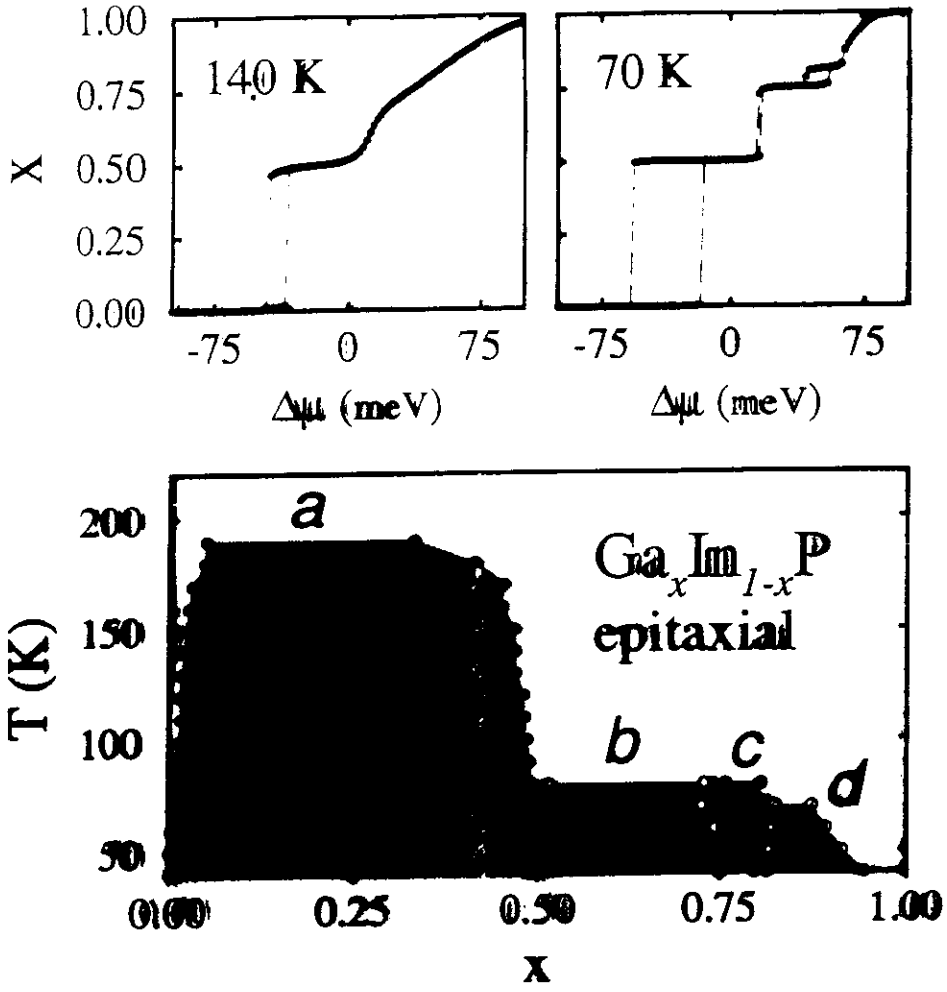
$$+ \underbrace{E(\{\sigma\},\Omega) - \left(xE_{Si}(\Omega) + (1-x)E_{Ge}(\Omega)\right)}_{\text{Configurational energy} = \frac{1}{2}\sum_{R-R'} \tilde{J}(R-R',\Omega)(\sigma_R \sigma_{R'} - 1)}$$

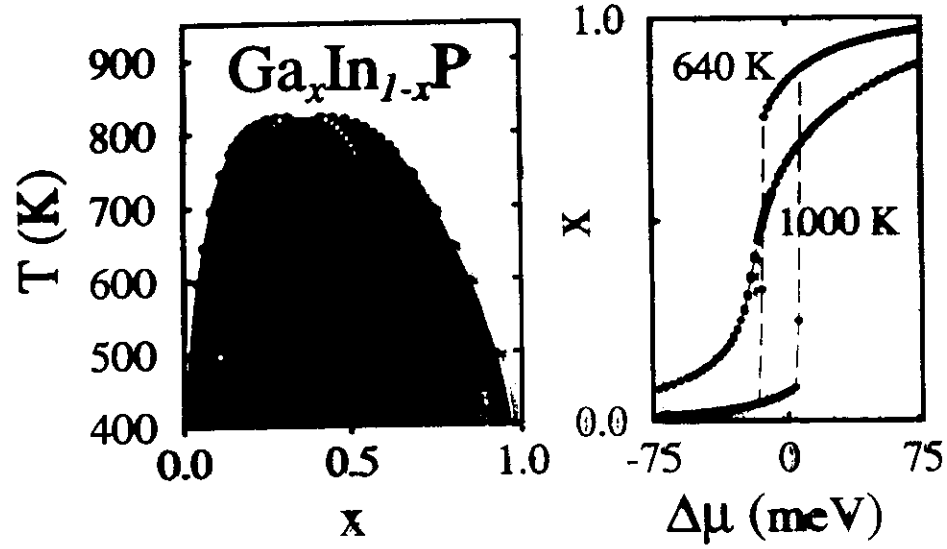
Metropolis random walk in $(\{\sigma\},\Omega)$ space:



$$\langle A \rangle_{TP\mu} \approx \frac{1}{N_c}\sum_c A\left((\{\sigma\},\Omega)_c\right)$$




1.00
0.75
0.50
0.25
0.00
x
140 K
70 K
-75
0
75
Δμ (meV)
200
150
100
50
T (K)
a
b
c
d
Ga$_x$In$_{1-x}$P
epitaxial
0.25
0.50
0.75
1.00
x


900
800
700
600
500
400
T (K)
Ga$_x$In$_{1-x}$P
0.0
0.5
1.0
x
1.0
0.0
x
640 K
1000 K
-75
0
75
Δμ (meV)